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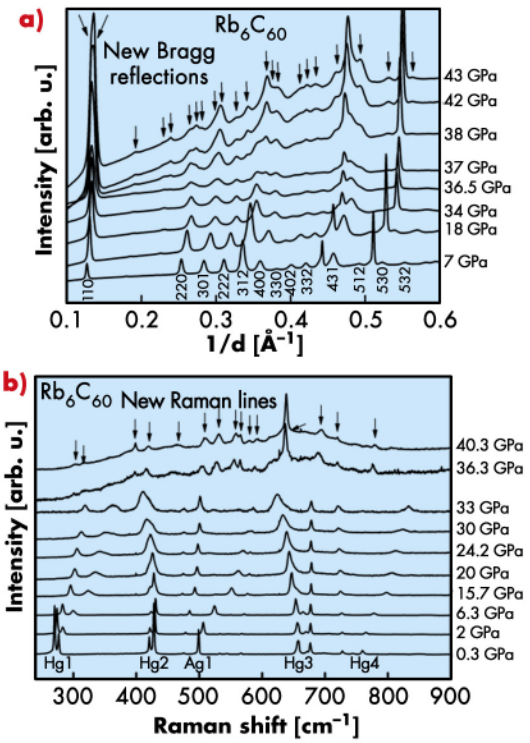

Fig. 116: **a)** Pressure evolution of XRD, and **b)** Raman measurements for Rb_6C_{60}. The occurrence of a phase transition at around 35 GPa is indicated by the appearance of new Bragg reflections and Raman lines, respectively.

occurs in cycloaddition processes characteristic of the C_{60} polymerisation. Hence, we suggest that the hexagonal HP phase could be associated to the formation of 2D polymers in the (001) plane of the hexagonal structure.

The lower pressure stability of the cubic phase (and of the molecular character) observed in Rb_6C_{60} compared to Cs_6C_{60} is concomitant with a more pronounced distortion of the molecule in the first compound compared to the latter. Nevertheless, both fullerides show a much higher pressure stability of the molecular character of the system, compared to the solid C_{60}. We therefore infer that the presence of such ionic host-guest interactions could be responsible for the high pressure stabilisation of the C_{60} molecules.

References
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Isotopic effect in extended X-ray absorption fine structure of germanium

Principal publication and authors
J. Purans (a,b), N.D. Afify (a), G. Dalba (a), R. Grisenti (a), S. De Panfilis (c,d), A. Kuzmin (b), V.I. Ozhogin (e), F. Rocca (f), A. Sanson (f), S.I. Tiutiunnikov (g) and P. Fornasini (a), *Physical Review Letters* **100**, 055901:1-4 (2008).
(a) Department of Physics, University of Trento (Italy)
(b) Institute of Solid State Physics, Riga (Latvia)
(c) Res. Centre Soft INFM-CNR, Roma (Italy)
(d) ESRF
(e) Res. Centre "Kurchatov Institute", Moscow (Russia)
(f) CNR-IFN and FBK-CeFSA, Trento (Italy)
(g) JINR, Dubna (Russia)

The structural, electronic and dynamical properties of crystals are mainly dependent on the atomic number of the constituent atoms. However, the isotopic composition has subtle but non-negligible influence on some basic properties, like density, phonon widths, and electronic energy gaps **[1]**. Isotopic effects are relevant not only for their basic scientific interest, but also for several possible technological applications **[2]**.

The dependence of the dynamical properties of crystals on the isotopic composition is of primary importance. The force constants depend on atomic species and crystal structure. However, the zero-point amplitude of atomic vibrations is also influenced by the nuclear masses, the lighter isotopes undergoing larger oscillations than the heavier ones. As a consequence of anharmonicity, the difference in zero-point amplitude of motion reflects on a difference of interatomic equilibrium distances and lattice parameters **[1]**. In the case of germanium, the expected relative change in the lattice parameter between ^{70}Ge and ^{76}Ge is as small as $\Delta a/a \approx 5 \times 10^{-5}$. Note that these effects, of genuine quantum origin, disappear progressively when temperature increases.

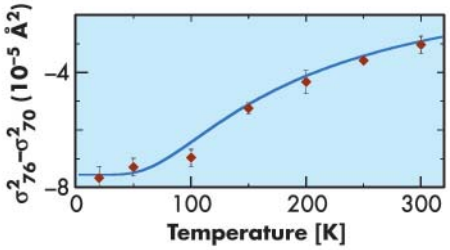

Fig. 117: Difference of the EXAFS MSRDs as a function of temperature for the two isotopes ^{70}Ge and ^{76}Ge. The solid line shows the difference between two Einstein models.

An investigation of the isotopic effect on the amplitudes of nearest-neighbours relative vibrations (parallel mean square relative displacement (MSRD)) and on the nearest-neighbours average distance in powdered samples of ^{70}Ge and ^{76}Ge has been performed by extended X-ray absorption fine structure (EXAFS) spectroscopy.

Two highly isotopically enriched Ge samples with the degrees of enrichment 98.2% for ^{70}Ge and 99.9% for ^{76}Ge were produced at the

Kurchatov Institute (Russia), and their Ge K-edge EXAFS spectra recorded with high accuracy from 20 to 300 K, at beamline **BM29**.

The difference of the MSRD values for two isotopes has been clearly evidenced (**Figure 117**) and is in good agreement with a behaviour expected from the Einstein model based on the single force constant k_0 = 8.496(40) eV/Å^2 and two characteristic frequencies: 7.70(2) THz for ^{70}Ge and 7.39(2) THz for ^{76}Ge.

The effect of isotopic mass has also been revealed in thermal expansion (**Figure 118**). The zero-point values of the nearest-neighbours average distance measured by EXAFS are consistent with the values of distance between average positions measured by Bragg diffraction, once the effects of vibrations perpendicular to the bond are taken into account. The possibility of detecting relative distance variations smaller than 10 femtometres by means of a conventional transmission EXAFS apparatus and a standard procedure of data analysis has been demonstrated.

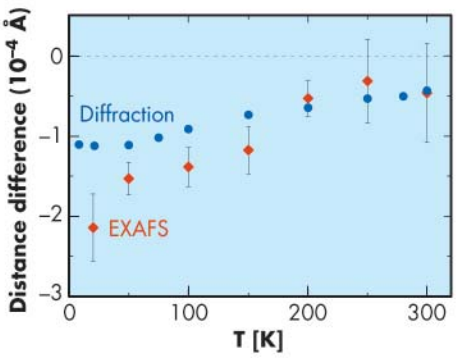

Fig. 118: Difference of the nearest-neighbour average interatomic distance in ^{76}Ge and ^{70}Ge, determined from EXAFS analysis (diamonds), compared with the difference of distances between average positions determined from X-ray backscattering (circles).

References
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In situ redispersion of platinum nanoparticles on ceria-based oxide for vehicle exhaust catalysts

Supported precious metals are used to facilitate many industrial catalytic processes. Platinum (Pt) in particular is used for the cleaning up of vehicle exhaust emissions. When the vehicle exhaust catalyst is exposed to high temperatures (~800°C and above), the highly dispersed metal nanoparticles agglomerate and sinter, decreasing the active surface area, which causes a loss of catalytic activity (*i.e.* deactivation). Exhaust gases exiting from gasoline engines change quickly during operation. Temperatures can rise transiently to around 1000°C and the exhaust gas composition itself fluctuates quickly between oxidative and reductive compositions. Hence, *in situ* dynamic observation on the sintering and redispersion phenomena of the precious metal in the automotive catalysts is very important indeed.

Real-time observation of the sintering/redispersion behaviour of Pt was made possible by the fluorescence yield variant (Turbo-XAS) of energy dispersive XAFS developed by Pascarelli *et al.* at **ID24** **[1]**.

An *in situ* cell optimised for fluorescence detection was designed for this experiment **[2]**. Fluorescence yield Turbo-XAS data collected at the Pt L_{III} edge on 2 wt% Pt/Ce-Zr-Y mixed oxide (referred to as CZY) catalysts under *in situ* conditions are shown in **Figure 119**. The signal to noise ratio on this data is improved with respect to our previous transmission XAS study on Pt/CZY, which showed that the combination of low levels of Pt in the catalysts, with high levels of heavy, absorbing, elements such as Ce and Zr severely compromises the conventional, transmission based experiments, making quantitative analysis very difficult **[3]**.

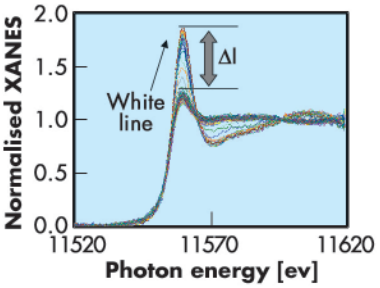

Fig. 119: Serial time-resolved Pt L_{III} edge XANES spectra (6 seconds each) of 2 wt% Pt/CZY catalyst under cyclical oxidising/reducing. Variation in the first hundred spectra under oxidising/reducing atmosphere at around 400°C.

Principal publication and authors
Y. Nagai (a), N. Hara (b), K. Dohmae (a), Y. Ikeda (b, g), N. Takagi (c, g), T. Tanabe (a), G. Guilera (d, h), S. Pascarelli (d), M.A. Newton (d), O. Kuno (e, i), H. Jiang (e), H. Shinjoh (a), S. Matsumoto (f), *Angew. Chem Int. Ed.* **47**, 9303 (2008).
(a) TOYOTA Central R&D Labs., Inc., Aichi (Japan)
(b) TOYOTA Motor Europe Technical Centre, Zaventem (Belgium)
(c) TOYOTA Motor Corporation Higashi-Fuji Technical Center, Shizuoka (Japan)
(d) ESRF
(e) TOYOTA Motor Engineering & Manufacturing North America, Inc., Michigan (USA)
(f) TOYOTA Motor Corporation, Toyota (Japan)
(g) Current Address: (f)
(h) Current Address: ALBA-CELLS, Barcelona (Spain)
(i) Current Address: (c)